IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

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SERIAL NO.:	10/570,553	GROUP:	Art Unit 4131
FILED:	March 3, 2006	DATED:	December 18, 2008

TITLE: NANOCOMPOSITE FIBERS AND FILMS CONTAINING POLYOLEFIN AND SURFACE-MODIFIED CARBON NANOTUBES

Mail Stop AMENDMENT
Commissioner for Patents
PO Box 1450
Alexandria, VA 22313-1450

Filed Via EFS-Web

DECLARATION UNDER 37 CFR § 1.131

Sir:

I, Benjamin S. Hsiao, do aver that I and my co-inventor conceived the claimed subject matter in the above-identified patent application prior to the filing date of U.S. Patent Application Publication No. 2004/0262581 (Serial No. 10/608,976) to Rodrigues ("Rodrigues").

The Rodrigues application was filed on June 27, 2003 and was published on December 30, 2004. However, I and my co-inventors conceived the claimed subject matter before June 27, 2003. In support thereof, I am attaching copies of a grant proposal which we prepared prior to June 27, 2003, which discloses the substance of the invention and forms the basis of the instant application. This grant proposal form clearly shows and supports the claimed subject matter in the instant application.

The first and second pages of the grant proposal, as well as the 4th page, identifies both myself and my co-inventor. (A Declaration from my co-inventor accompanies this Declaration.)

Page 6 of the grant proposal clearly describes carbon nanotubes and nanofibers, as well as modified carbon nanotubes and incorporating the modified carbon nanotubes or nanofibers into rigid-chain polymers and polyolefins.

Pages 17-21 of the grant proposal (numbered 10-14, respectively, at the bottom of the pages) include more detail regarding the modification of the carbon nanotubes or nanofibers and incorporating the same in polyolefins. Graphical depictions of these modifications are included, for example on pages 18 (numbered page 11 on the bottom of the page) and 19 (numbered page 12 on the bottom of the page).

Descriptions of the generation of data regarding the morphology and crystal structure of the materials is described in the last paragraph of page 21 (numbered page 14 on the bottom of the page); such data is included, for example, in Figures 6, 7, and 9-11 of the application as filed. The drawings and written description clearly support the claimed subject matter of the instant application.

Furthermore, the grant proposal was prepared and submitted before June 27, 2003 and clearly demonstrates a conception before the filing date of Rodrigues. Subsequent to the conception of the subject matter, I and my co-inventor worked diligently with patent counsel in preparing and filing U.S. Provisional Patent Application No. 60/500,812 on September 5, 2003, followed by filing the International Application on which this application is based. (The International Application was filed on September 3, 2004; the instant application has a 35 U.S.C. 371(c)(1) date of March 3, 2006.) As part of preparing the Provisional and International Applications for filing, I and my co-inventor reviewed and commented upon the draft application and drawings.

Therefore, for at least the foregoing reasons, the Rodrigues patent is not prior art to the

instant application and cannot be applied against the claimed subject matter.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the above-referenced application or any patent issued thereon.

Respectfully,

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Benjamin S. Hsiao

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EXHIBIT

Benjamin   Chu

Benjamin S Hsiao

| Benjamin Chu |
| Benjamin S Hsiao |

The strongest known lightweight material on a microscopic scale is the carbon nanotube. The strongest lightweight fibers are made from rigid-chain polymers, such as poly(p-phenylene terephthalamide) [PPD-T, known as Kevlar], poly(p-phenylene benzobisoxazole) [PBO, known as Zylon], or from long flexible-chain polyolefins, such as ultra-high molecular weight polyethylene [UHMWPE, with fibers known as Spectra or Dyneema].

modified carbon nanotubes or nanofibers can be incorporated into rigid-chain polymers such as PPD-T and PBO, and   modified carbon nanotubes can be incorporated into long flexible-chain polyolefins such as UHMWPE and UHMWPP (polypropylene).

For example, the modifications of carbon nanotubes have to take into account of several key factors: (a) the chemical nature and molecular architecture of the side-chain modifiers, both at the tube ends and at the side-wall, and (b) the space packing of carbon nanotubes, either in the polymer matrix or in the presence of only coupling or crosslinking agents.

oxidized carbon nanotube can be performed by the reaction with an amine modifier bearing an oligomer unit with a terminal cap such as m-Kevlar-NH$_2$, m-PBO-modifiers will be prepared through step wise condensations using the corresponding 1,4-diaminobenzene, 2,4-diamino-1,5-dihydroxybenzene, 2,3,5,6-tetraaminopyridine, and terephthalic acid monomethyl ester (or its monoacid chloride) or 2,5-dihydroxyterephthalic acid monomethyl ester, starting from benzoic acid that acts as terminal cap for m-Kevlar-NH$_2$, m-PBO-NH$_2$, m-PIPD-NH$_2$.

The reactions of these amine modifiers with oxidized carbon nanotubes using the EDC coupling or acid chloride method should give the corresponding surface and terminal modified carbon nanotubes. In a similar manner, the reactions of these modifiers with carbon nanotubes bearing sulfonic acid groups should yield the corresponding sulfonamides by dehydration by simple mixing and heating.
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nanocomposites of iPP and PBO with the corresponding modified carbon nanotubes.

As mentioned above, the carboxylic acid density in the oxidized carbon nanotubes ranges from 1 to 7 % of the total surface area   , and higher density of carboxylic acid and sulfonic acid groups can be realized by oxidation using a sulfuric acid/nitric acid combination   . If all carboxylic acid groups (and sulfonic acid groups) are modified, these straight chain (i.e., single-tethered) modifiers should be able to cover the vast majority of the carbon nanotube surface provided that the oligomer units are aligned parallel to the surface when blended with polymers.

double-tethered modifiers using the single-tethered modifiers described above and benzenetricarboxylic acid linkers   . 1,3,5-Benzenetricarboxylic acid and 1,2,4-benzenetricarboxylic acid anhydride are commercially readily available. One of the carboxylic acids will be connected to an alkylidenediamine to secure an amine terminus for modification of nanotubes.

An alternative synthetic approach will be used for surface modification of the carbon nanotubes to make them suitable for combination with poly(olefin) polymers such as PE, PP, and fluoropolymers. In this case a "grafting from" approach will be used. The proposed chemistry will involve attachment of a polymerization initiator to the surface of the carbon nanotubes, by reaction with surface carboxylic acid functions. The advantage of this approach is that once the initiator attachment process is optimized, any variety of polymers of predetermined molecular weight can be placed on the nanotube surfaces.

Living radical polymerization (LRP) will be used to form the grafted polymers, since many grafts of interest can be produced using this initiation method. This method will be used in preference to anionic polymerization, because of the versatility of LRP and the greater number of monomers that can be polymerized. Living radical polymerization falls into two general classes, one of which is suitable for styrenic   and diene monomers   (nitroxide) and the other of which is best suited for methacrylate monomers (Cu-bipyridine)   . Polymer grafts of narrow molecular weight distribution up to 50,000 g-mol^{-1} can be produced. Both methods can be used to initiate polymer formation by attachment of small molecules to the surface functionalized carbon nanotubes. Hydroxy-functionalized initiators for the diene polymerization will be produced from TEMPO and other nitroxides that permit lower reaction temperatures and these groups will attached to the carbon nanotubes in varying density to influence the compatibility

Formation of grafts that are suitable for blending with polyolefins will be carried out by polymerization of butadiene and isoprene. It will be necessary to hydrogenate the resulting polydienes using conventional hydrogenation reactions. Simple medium-pressure reactors capable of carrying out this reaction are available to us. We will use both supported and soluble catalysts for reduction of the double bonds. Hydrogenation of poly(butadiene) will produce linear PE grafts while reduction of poly(isoprene) will form the equivalent of poly(ethylene-r-propylene), the latter being suitable for use with the PP matrix. These reaction steps are shown   The effect of polymerization and hydrogenation will be monitored by removal of the grafts via hydrolysis of the binding ester function.
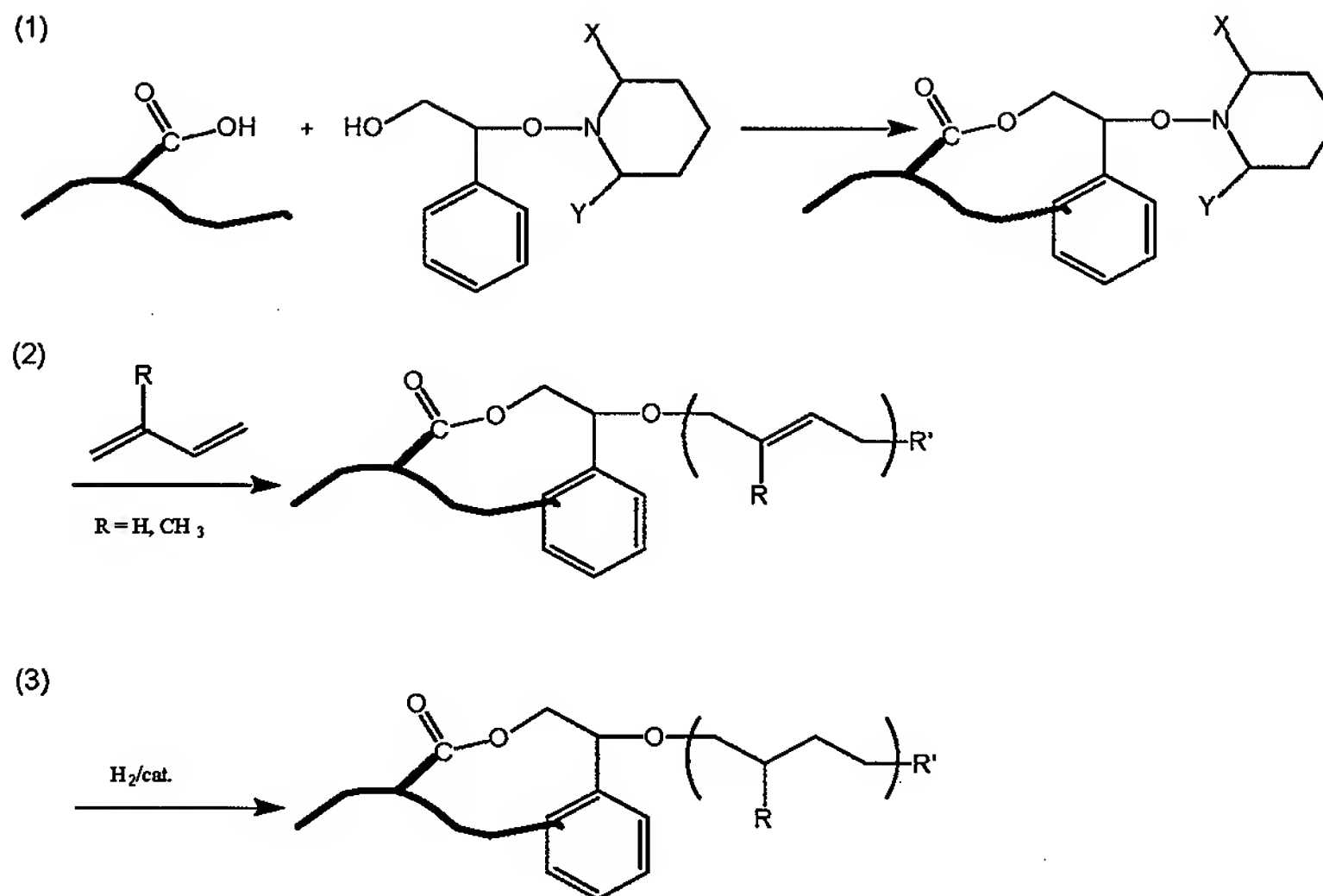
As the chemistry for modification of the ethylene chains is relatively difficult, we will emphasize the modification of UHMWPP for this study. The unique feature of propylene polymerization, versus the polymerization of ethylene, is the symmetry of the monomer insertion into the growing chain. The "stereospecificity" of the polymerization can broadly be categorized into three types: isotactic, syndiotactic, and atactic. In addition to these limiting tacticity types, the monomer has a head and a tail. Specificity relating to the monomer orientation is termed "regiospecificity". Virtually 100% of the commercial production of polypropylene is based on the regio-regular isotactic polypropylene produced by Ziegler-Natta catalysts.

Historically, UHMWPP has received less interest at the industrial level than UHMWPE. This is due to the poorer impact and abrasion resistance of UHMWPP relative to UHMWPE in melt processing applications, as well as the expected lower crystal modulus of the iPP helix relative to PE in highly drawn fiber applications. It should be noted, however, that rigorous comparisons at comparable degrees of polymerization are lacking, and for ballistic applications, there is no reason to believe that the PE chains will be more resistant than the PP chains. UHMWPP is not produced commercially at degrees of polymerization comparable to UHMWPE. Additionally, the evolution to fourth and fifth generation Ziegler-Natta catalysts for iPP have focused on improving the activity (limiting the need for de-ashing steps) and compatibility (related to particle morphology) with modern high volume production processes.

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We believe the UHMWPP sample with viscosity average molecular weights approaching 5 million (degree of polymerization ~ 120,000) is possible in the absence of hydrogen provided the polymerization temperature is sufficiently low. These molecular weights will approach, but do not reach, that of commercial UHMWPE.

The ability to create radical sites along the polymer backbone is an essential condition for free radical functionalization/grafting chemistry. The PP modification has been most common, while carbon nanotubes can lead to superior mechanical performance (e.g., toughness and tenacity), higher heat distortion and end-use temperatures and improved fire retardation in the final products.
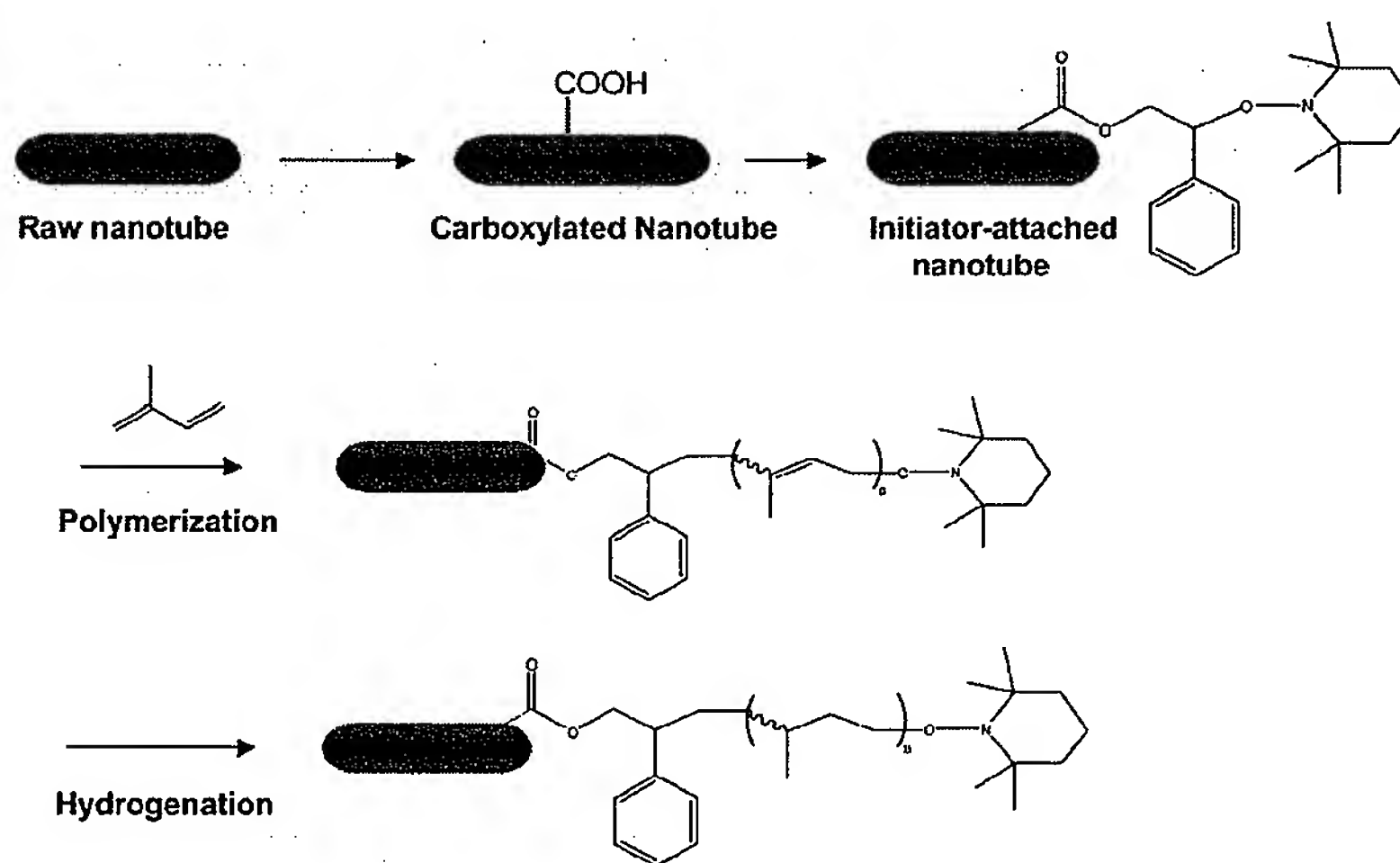
The attachment of TEMPO-based initiator to the carboxylic groups of SWNTs is being carried out by using a typical coupling agent, dicyclohexyldicarboimide (DCC) . It is a one-step synthesis. We plan to use poly(ethylene-*co*-propylene) as a compatibilizer for SWNT and iPP. Solution polymerization of isoprene and hydrogenation

of poly(isoprene) should be optimized for synthesizing poly(ethylene-*co*-propylene).

We plan to purchase vapor grown carbon nanofibers such as Pyrograf III (PR-21-PS) from Pyrograf Products Inc. (Cedarville OH). These fibers will be first chemically modified using the synthetic schemes outlined earlier   and then be dispersed in the polymer matrix using

For this purpose, combined rheology and synchrotron X-ray experiments will be carried out to study the flow-induced structural changes in conditions similar to real processing. We plan to carry out studies under three types of flow conditions: (1) a steady-state shear, (2) an oscillatory shear, and (3) an elongational flow. We will use the modified parallel-plate shear apparatus (Linkam CSS 450 Optical Shearing System, **Figure 1**) to study the steady-state shear experiment and a Rheometric Solids Analyzer (RSA-SL, **Figure 1**) to study the oscillatory shear experiment. The oscillatory shear measurement is a novel new experiment designed to explore the dynamic nature of flow-induced crystallization. The proposed experimental procedures are as follows. As the oscillatory deformation is applied (at a suitable frequency and strain ratio), the X-ray data will be collected simultaneously at a rate synchronized with the frequency of the dynamic shearing (for example, if the frequency for the oscillation shear is 1 Hz, then the image collection time will be 0.5 s). In this case, the SAXS/WAXD images will be collected exactly in-phase and out-of-phase with respect to the applied deformation. If sufficient images (say 200 frames) are collected, Fourier transformation of the structural and morphological parameters (determined from the SAXS or WAXD images) along the *time domain* can be calculated. As a result, the parameters can be deconvoluted into the real (reversible) and the imaginary (irreversible) components. The achievable frequency range for this experiment will be from 10^{-5} to 1 Hz. This measurement shall reveal new information about the structural changes induced by an oscillatory shear, which has never been done before. The information from this experiment is directly related to the viscoelastic properties of the material system, especially with elastic behavior.

Although our preliminary *in-situ* fiber study of rigid-chain polymers (PBO) successfully determined the physics of the dry-jet wet-spinning process before coagulation, the coagulation process itself has yet to be characterized in a similar fashion and the spinning process has not been fully optimized to obtain the ideal structure. Given the importance of coagulation in the processing of lyotropic LCPs (PBO, PIPD and PPD-T) and their mixtures with carbon nanotubes into fibers and films, it would be useful to gain an in-depth knowledge of the formation of microfibrillar microstructures as a function of mixing time, extrusion/spinning temperatures, and line tension during both dope conditioning and fiber spinning in order to optimize the processing of these materials. We will address the spinning process by coagulation using *in-situ* simultaneous X-ray scattering and diffraction experiments, together with Raman spectroscopy. Mechanical processes such as mixing (dope conditioning), extrusion and spinning are the most practical and cost effective ways to manipulate the structural formation in fibers.

The properties of high-strength fibers are directly related to the development of molecular orientation in the draw zone under extensional flow conditions. Although the final properties and microstructure of the fibers can be evaluated after processing is completed, it is desirable to understand the development of molecular orientation *in-situ* during spinning and drawing. This study will be carried out using a custom built *in-situ* fiber spinning device which has recently been used to investigate the filaments produced from a liquid crystalline PBO dope in polyphosphoric acid.

The gel spinning technique has been used successfully for production of ultra-high molecular weight polyethylene (UHMWPE) fibers. We plan to adopt and modify the conventional gel spinning procedures in order to produce advanced nanocomposite fibers containing modified carbon nanotubes (or carbon nanofibers) and modified UHMWPE matrix. Morphology and mechanical properties of the fibers will be controlled by varying the extrusion conditions during fiber formation and by stretching. A range of fiber drawing temperature from 100-130 °C together with different draw ratios will be used to optimize the fiber properties. The structural development during these processes will be monitored by *in-situ* Raman spectroscopy, synchrotron X-ray scattering and diffraction techniques.

We plan to use 2D simultaneous WAXD and SAXS setup to study the, nanostructural morphology, crystal structure and microphasic behavior of as-spun nanocomposite fibers with carbon nanotubes using the tensile stretching apparatus or the continuous fiber draw apparatus at various annealing temperatures. The stake in understanding the fiber post-spinning processes (stretching and annealing) is high, because it has direct impacts on the final properties. In a way, molecular orientation, as measured by crystalline and non-crystalline orientation functions is a key morphological parameter that governs the properties of LCPs and UHMW polyolefins (mechanical properties, degradation performance). The observed WAXD patterns can be used to yield direct information on crystal structure, unit cell parameters and crystal orientation, the SAXS pattern can yield information on the nanoparticle arrangement, lamellar morphology and crystal fibrils.